

## Development of metal cluster-based energetic materials at NSWC-IHD

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# DEVELOPMENT OF METAL CLUSTER-BASED ENERGETIC MATERIALS AT NSWC-IHD

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**Abstract.** Current research efforts at NSWC-IHD are utilizing gas-phase molecular beam studies, theoretical calculations, and condensed-phase production methods to identify novel metal cluster systems in which passivated metal clusters make up the subunit of a molecular metal-based energetic material. The reactivity of  $\text{Ni}_x\text{Al}_y^+$  clusters with nitromethane was investigated using a gas-phase molecular beam system. Results indicate that nitromethane is highly reactive toward the  $\text{Ni}_x\text{Al}_y^+$  clusters and suggests it would not make a good passivating ligand for these cluster systems. To date, small amounts of a metal-based compound with a subunit containing four aluminum atoms and four Cp\* ligands has been produced and was characterized using DSC and TGA. Results indicate this cluster material is more reactive than micron- and nano-sized aluminum. However lack of stability in air precludes it from being a viable replacement for current aluminum particles. Volumetric heat of combustion of  $\text{Al}_{50}\text{Cp}^*_{12}$  was determined using thermodynamic data obtained from first principles calculations. The  $\text{Al}_{50}$  cluster is found to have a heat of combustion near 60% that of pure aluminum.

**Keywords:** Metal Clusters, Thermodynamics, Gas-phase reactivity, Aluminum.

**PACS:** 81.16.Be, 81.70.Pg, 82.30.Fi, 82.20.Wt.

## INTRODUCTION

The energy available from the combustion of aluminum is more than that of conventional high explosives and as a result is often loaded into explosive and propellant formulations in micron and nano particle form [1-3]. However, the rate of energy release from combusting aluminum particles is significantly lower than that of CHNO explosives such as TNT and RDX. In order to realize faster reaction rates, the size of the particles of interest need to be reduced significantly into the molecular size-range (10's of atoms). Small air-stable clusters containing tens of metal atoms

protected by passivation ligands are ideally suited to fill this gap.

One of the major hurdles in the development of new cluster based materials is selection of passivating ligands to prevent oxidation in air. These passivating ligands need to be designed to minimize parasitic weight while providing either an oxidizer or an energetic material in close proximity to the metal cluster. While a multitude of potential energetic ligands currently are known, their use as passivating agents for clusters is relatively unexplored.

The results reported here are from a multi-faceted effort to develop novel metal cluster-based

energetic materials for next generation propellants and explosives. A combination of gas-phase molecular beam studies, theoretical calculations, and condensed-phase production methods are implemented, and the results from these initial efforts are presented.

## EXPERIMENTAL PROCEDURE

### Gas-Phase Experiments

The gas-phase work presented here was performed using a previously described cluster beam apparatus designed for the study of gas-phase cluster ion reactivity [4]. Briefly, the instrument is composed of the following systems: the magnetron ion source, a differentially pumped quadrupole ion guide, a mass selection quadrupole mass filter, a collision region comprised of a hexapole ion guide and a second quadrupole mass filter for final detection of reaction products.  $\text{Ni}_x\text{Al}_y$  cluster cations were produced by sputtering a  $\text{Ni}_x\text{Al}_y$  target (50/50 wt.%, ACI Alloys, Inc.) in the magnetron cluster source (Oxford Applied Research). Reactive gas species were introduced to the vacuum in dilute mixtures of He through a gas inlet system. The reactive gas mixtures used included a 25%  $\text{O}_2$  in He mixture and a 5% nitromethane in He mixture.

### Condensed-Phase Experiments

Aluminum monohalide,  $\text{AlX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ ), solutions were produced using a method outlined by Dr. Hansgeorg Schnockel [5]. Briefly,  $\text{AlX}$  vapors are generated inside a bell jar cooled to  $-196^\circ\text{C}$  using a specially designed furnace that percolates anhydrous  $\text{HX}$  gas up through graphite crucibles containing pools of liquid Al at  $\sim 850^\circ\text{C}$ . By controlling the  $\text{HX(g)}$  flow rate, one can entropically drive the equilibrium completely to the monohalide side. The  $\text{AlX}$  molecules are then co-condensed with solvent on the inner walls of the reactor over a 3-4 hr. period. The  $\text{AlX}$  / solvent matrix is then warmed to  $-78^\circ\text{C}$  to generate metastable solutions of  $\text{AlX}$  that are stable at low temperatures for months.

The  $\text{AlBr}$  solution produced was then reacted under previously described conditions to produce the  $\text{Al}_4\text{Cp}^*_4$  cluster material [6]. The resulting yellow crystals were identified as  $\text{Al}_4\text{Cp}^*_4$  using NMR and subjected to Differential Scanning

Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) to investigate thermal properties of the cluster materials.

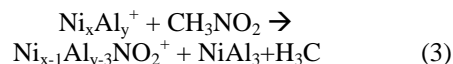
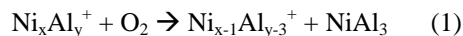
## Theory

First-principles calculations were performed on the large cluster/ligand systems to examine their stability and possible combustion properties. All-electron calculations were performed using the B3LYP density functional and a 6-31G(d,p) basis set. This combination gives accurate thermodynamic values (as compared to G2 calculations on smaller clusters) while still being efficient enough to calculate structures and accurate vibrational properties of the large clusters (350+ atoms). Thermodynamic data was used to calculate the volumetric enthalpy of combustion in air.

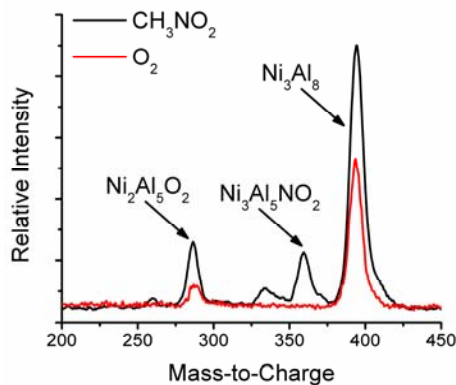
## RESULTS AND DISCUSSION

### Gas-Phase

The majority of  $\text{Ni}_x\text{Al}_y$  clusters investigated proved to be reactive toward both  $\text{O}_2$  and  $\text{CH}_3\text{NO}_2$ . The cluster reactivity is characterized primarily by decomposition rather than adduct formation. Representative mass spectra containing both the parent cluster and the reaction products for  $\text{Ni}_3\text{Al}_8^+$  are shown in Fig. 1. Interestingly, the oxidation of  $\text{Ni}_x\text{Al}_y$  clusters was found, in most part, to proceed through a common mechanism involving the addition of an  $\text{O}_2$  molecule and a subsequent loss of  $\text{NiAl}_3$ . Previous density functional theory (DFT) calculations have shown that  $\text{NiAl}_3$  is a very stable tetrahedral structure [7]. In addition to oxidation by  $\text{O}_2$ , the reactivity of  $\text{Ni}_x\text{Al}_y^+$  clusters with nitromethane was found to produce the same  $\text{Ni}_x\text{Al}_y\text{O}_2^+$  reaction product. These peaks also show that nitration of the cluster occurs. The following reaction pathways 1-3 are suggested to describe the peaks observed in Fig. 1.



These reaction pathways can be used to describe products observed for all the  $\text{Ni}_x\text{Al}_y^+$  clusters investigated here.

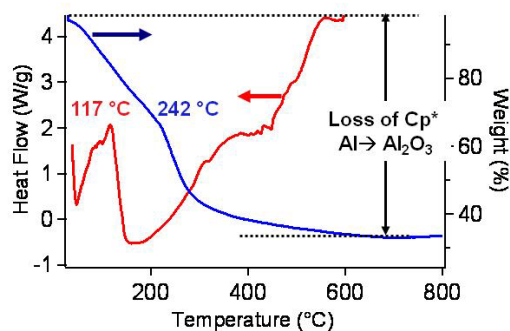


**Figure 1.** Mass spectra of the products detected during the reaction of  $\text{Ni}_3\text{Al}_8^+$  with oxygen (red) and nitromethane (black). The parent peak along with prominent product peaks, such as  $\text{Ni}_2\text{Al}_5\text{O}_2^+$ , is shown.

#### Condensed-Phase

A small amount of  $\text{Al}_4\text{Cp}^*_4$  (~20 mg) was produced using a previously published method [5]. The small yellow crystals were found to be stable for up to 30 minutes when exposed to air after which a slow oxidation process was observed. Time-resolved optical microscopy was performed on the crystals and revealed small brown colored inclusions in the crystals. These inclusions were found to become colorless over 30 min. It was determined these inclusions were trapped AlBr precursor and illustrated the need to improve the crystallization process. The remaining sample was analyzed using DSC and TGA. Results from this analysis are shown in Fig. 2. The DSC trace shows an exotherm at 117 °C followed by a steady rising exotherm. The initial feature at 117 °C is attributed to combustion of the  $\text{Cp}^*$  ligands followed by a slow combustion of the remaining Al containing material. The initial decomposition occurs at a significantly lower temperature than current CHNO explosives, PETN (163 °C) [8]. The TGA trace, shown in Fig. 2, displays an almost linear decrease in weight starting around 100 °C followed by a sudden increase in weight change around 242 °C. By 600 °C 65% of the original weight has been lost. This type of decomposition behavior is

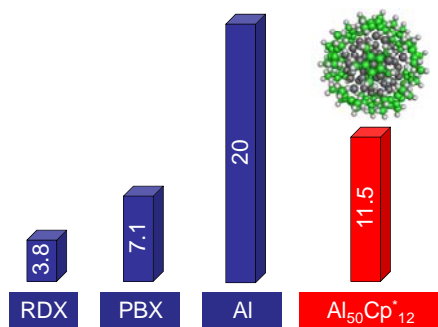
significantly different compared to oxide coated nano-aluminum in which a constant increase in weight due to oxidation is observed [9]. However, the observed decomposition behavior is similar to perfluoroalkyl coated nano-aluminum produced by Dr. Jason Jouet [3]. The measured weight loss was found to represent the loss of all  $\text{Cp}^*$  and complete oxidation of the aluminum cluster core. While this analysis needs to be repeated, the current results suggest this cluster material combusts at a significantly lower temperature than pure aluminum or even coated nano-aluminum.



**Figure 2.** Differential Scanning Calorimetry and Thermal Gravimetric Analysis data collected from the  $\text{Al}_4\text{Cp}^*_4$  cluster material.

#### Theory

Our calculations on aluminum-cyclopentadiene type cluster materials confirm that these materials have significant energy density and likely very rapid combustion kinetics. An analysis of the bond strength in larger clusters indicates that the most likely initial step in unimolecular thermal decomposition is the loss of surface  $\text{AlCp}$  or  $\text{AlCp}^*$  units, exposing the strained interior aluminum core. The calculated enthalpies of combustion for these materials are high, approaching 60% that of pure aluminum. This value for  $\text{Al}_{50}\text{Cp}^*_{12}$  is shown in Fig. 3 along with the heats of combustion of bulk aluminum, RDX, and a typical aluminized plastic bonded explosive denoted PBX. These materials thus offer high energy densities but with the possibility for extremely rapid kinetically-limited aluminum combustion.



Heat of combustion (kcal/cm<sup>3</sup>)

**Figure 3.** Calculated volumetric heat of combustion of various energetic materials and formulations compared to the Al<sub>50</sub> cluster.

### CONCLUSIONS

Current efforts underway at NSWC-IHD to produce cluster based energetic materials were presented. Gas-phase studies investigating the use of nitromethane as a passivation ligand along with alloy effects were introduced. Oxidation and nitration decomposition pathways were observed; however CH<sub>3</sub>NO<sub>2</sub> adducts were not observed. Nitromethane, while exhibiting unique and diverse reaction pathways with all Ni<sub>x</sub>Al<sub>y</sub> clusters, proved to be an inadequate passivating agent for Ni<sub>x</sub>Al<sub>y</sub> cluster cations. Although further study is required, the data presented here represents a significant step toward understanding the stability and reactivity of Ni<sub>x</sub>Al<sub>y</sub> clusters under ambient and post-detonation environments. In an effort to produce gram quantities of energetic cluster materials a Al<sub>4</sub>Cp\*<sub>4</sub> cluster material was produced using a previously reported method. The resulting material showed increased reactivity relative to micron and nano aluminum. However, this material was not air-stable enough to be considered a replacement for current aluminum particles. The volumetric heat of combustion was calculated for Al<sub>50</sub>Cp\*<sub>12</sub> and found to be significantly higher than RDX and current aluminized PBX formulations. Work toward the synthesis of the Al<sub>50</sub> cluster is currently underway for comparison to these calculations. Further work to produce a stable metal-based cluster material designed for next generation propellants and explosives is also currently underway.

### ACKNOWLEDGEMENTS

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